

LABELING WITH POLYMERIC LABELS HAVING AN ACTIVATED HYDROPHILIC LAYER

FIELD OF THE INVENTION

- 10 This invention relates to polymeric sheets or rolls particularly adapted for use as labels in the post mold labeling of plastic, glass or metal containers or surfaces. More particularly, the present invention relates to polymeric film substrates adapted for printing
- 15 that also have a hydrophilic surface layer activatable into an adhesive layer for use as labels in post mold labeling applications using conventional wet applied water based labeling equipment typically used for the application of paper labels. In another aspect the
- 20 invention relates to such labels which possess the beneficial properties of the known plastic label substrates, but which are able to be applied on conventional post mold paper labeling equipment using wet applied water based solutions comprising water, water
- 25 blended with a selected cross-linking agent, adhesives or adhesives blended with a selected cross-linking agent.

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BACKGROUND OF THE INVENTION

Plastic and glass containers or bottles are prevalent in a wide variety of shapes and sizes for holding many different types of materials such as detergents, chemicals, motor oil, beer, etc. These containers are glass or plastic (mono or multi layers) of polyethylene, polypropylene, polyester or vinyl along with other specialty blends for specific barrier and product resistance performance. Generally such containers are provided with a label which designates the trade name of the product and may contain other information as well. The early art which still is prevalent today employed the use of labels manufactured from paper substrates that were applied with a water based adhesive. Subsequently, dry pressure sensitive self adhesives and in mold labels manufactured from paper have been and continue to be used. The shortcomings of paper labels with regard to tearing, wrinkling, creasing and the like due to age and moisture, or due to a lack of deformability when applied to a deformable plastic substrate have been well documented in the labeling industry. Because of this and the need to produce recyclable plastic containers, over the years a great deal of effort has been expended to develop container decoration techniques and durable film substrates which would overcome these shortcomings.

Polymeric film facestocks for container decoration which have resulted from these efforts can be applied to glass and plastic containers as self adhesive pressure sensitive labels as described in the prior art. The use of self adhesive paper and film "pressure sensitive adhesive" (PSA) labels that have been preprinted and

- 5 supported on a release liner is not a cost effective
option because of the added cost of the release liner
used to support and render processable the self adhesive
face stock. The cost of this type of structure combined
with the added cost of disposal of the liner does not
10 make pressure sensitive labeling a desirable option from
an economic or environmental standpoint for high volume
applications. In addition, PSA labelers typically run
much slower than cold glue labelers and capital
investment in new labeling equipment is required to
15 transition from wet applied Post Mold Labels (PML) to
self adhesive PSA labels. Also a factor is the effect of
a new process on an existing packaging line in terms of
learning curve and experience.
- 20 Another film face stock labeling technique that has
evolved is the use of heat activated in-mold labels as
described in the prior art where a preprinted plastic
label with a heat activated adhesive is placed in the
mold before the molten plastic resin is injected or blown
25 into the mold cavity at elevated temperature and pressure
which activates the adhesive and fuses the label
substrate to the container in-mold resulting in a pre-
decorated container as it exits the mold.
- 30 The use of polymeric film based in-mold label substrates
presents a more cost effective alternative than self
adhesive pressure sensitive labels in terms of substrate
cost but as this technology has progressed, it has been
found that productivity is impacted by the label feeding
35 step into the mold which is performed in a complex,
continuous and rapid manner which results in large
amounts of scrap material. Also, the initial capital

5 investment required to tool up for a container specific
in-mold label process for new molds and the complex
electromechanical maintenance intensive feeding devices
is significant. Another detriment for this process is the
potential inventory carrying costs for varieties of
10 labeled containers that come into play with predecorated
containers such as in-mold for those who would choose to
apply the label immediately pre or post filled.

Post mold decoration of glass and plastic containers in
15 the current art can also be accomplished by direct screen
printing on the container. Direct screen printing on the
container is not a cost effective process and also
presents the aforementioned inventory problems along with
added cost for freight to and from a screen printer. The
20 graphical possibilities for label copy are limited in
terms of cost and quality with this technique. Commodity
products can not support the cost of this labeling
technique.

25 Another post mold technique that has been popular is the
"Therimage" process. This process transfers a reverse
printed image from a transfer release sheet under
temperature and pressure to produce decorated containers.
The "Therimage" technique of transferring a reverse
30 printed image is costly because of transfer sheet costs
and presents the same disposal problems and costs with
the transfer sheet as occurs with the aforementioned
release liner used in conjunction with self adhesive
labels. Graphic design and quality is limited with this
35 technique.

Other techniques for labeling various plastic and glass
containers with preprinted paper or film label substrates

5 include the use of hot melt adhesives (not aqueous) which
are applied to the label substrate or container in a
molten state with container and substrate subsequently
married while the hot melt is molten. When the hot melt
adhesive cools, it sets up and bonds the label substrate
10 to the container. This technology requires the use of
sophisticated melting and application equipment that must
be operated, cleaned and maintained at elevated
temperatures. This technology works well with complete
360 degree wrap around labels but has not evolved to the
15 point to allow consistent labeling of a die cut or square
cut label with less than 360 degree wrap. Affixing a cut
label to an area on a container with 100% or patterned
adhesive application using hot melt adhesives has not
been commercially perfected. Complete wrap around hot
20 melt applied labels where one end of the label is affixed
to the container while the other end is wrapped around
the container and affixed with hot melt to the label
substrate is proven hot melt label application technology
that works well for film and paper label substrates. This
25 technology does not fit for individually labeled panels
on a container such a rectangular oil, contoured
detergent or beer containers where discrete labels are
applied such as a neck label, front label or rear label
that are not wrapped around 360 degrees. Another drawback
30 is the added cost for label substrate when this technique
is used since more label substrate is required because of
the 100% wrap around.

Lastly, one of the oldest and still prevalent labeling
35 techniques is the application of paper based labels to
glass and plastic containers using natural and synthetic
labeling adhesives such as BL300 produced by Henkel
Adhesives or OC363-20 produced by O.C. Adhesives Corp.

5 which are known in the art. This is a safe (water based)
proven technology that has grown and been employed for
many years and consequently there are many existing
machines that have been installed for this type of
labeling technique such as from Krones, Neutraubling,
10 Germany that run cut precut labels or Koyo, Japan which
runs roll stock that is cut on machine to the label size.
The cut label techniques and associated adhesives work
well with paper based substrates applied to glass,
plastic or metal containers because the wet adhesive
15 wicks (absorbs) into the paper substrate from the
applicator roll, pad or pallet which breathes and allows
the moisture from the water carrier to be absorbed by and
dry thru the paper base.

20 This technique obviously will not work well with non-
porous polymeric substrates as the adhesive can not wick
into the polymeric substrate for initial tack and
adhesive transfer to the label or drying thru the
plastic. Typically, wet applied cut label machines work
25 where glued pallets rotate and come in contact with a
glue applicator roll and become wetted with adhesive. The
adhesive wetted pallet then is pressed in contact with
the back side of the paper label where the adhesive
penetrates the paper fiber with enough initial tack to
30 remove the label out of the label holding magazine while
simultaneously gluing the back side of the label. This is
accomplished by applying a thin glue film to the pallet
picked up from the applicator roll metering system in a
pattern or with 100% coverage which is then pressed in
35 intimate contact against the first label in the stack.
The glue roller and pallet systems in the current art
typically employ a steel glue roller and a hard rubber
pallet with a durometer greater than 60 or a rubber glue

5 roller and an aluminum or coater steel pallet. Either combination provides for a firm pallet to transfer the adhesive.

After its removal, the label sticks on the entire glued
10 area of the pallet until transferred to a "gripper" cylinder and removed from the pallet typically using a vacuum mechanism. The gripper cylinder then transfers the label to the container to be labeled. The various machine designs and techniques are well known within the labeling
15 industry and to those skilled in the art. The "Krones Manual Of Labeling Technology" by Hermann Kronseder dated December 1978, is hereby incorporated by reference.

In recent years, as described in U.S. 6,663,746 and 6,517,664, which are incorporated by reference, polymeric
20 film labels using a hydrophilic glue receptive layer and a water based adhesive composition are now being used. The applications also describe the concept of rewetting the hydrophilic layer with an aqueous medium (water or adhesive that may contain a cross-linking agent) to
25 activate the hydrophilic layer into an adhesive layer.

Attempts have been made to use polymeric substrates with high moisture vapor transmission rates (MVTR) and tacky or pressure sensitive adhesive on conventional labeling equipment with little success. The tacky adhesive
30 required to stick to the water impervious polymeric substrate causes machining problems by gumming up the adhesive application system and creates cleanup issues. The high MVTR substrates also did not have good wet tack with existing commercially available adhesives that would
35 machine without problems and did not dry rapidly enough making the labels prone to "swimming" or moving from the desired application area during down stream processing.

5 In addition, the adhesives do not wet out and apply
uniformly to non hydrophilic surfaces with the crude
adhesive metering and application systems currently in
use on existing paper labeling machinery. Without uniform
application, wet out and wet tack, it will be impossible
10 to apply a clear label that has the no label look because
of adhesive and application imperfections. Recent
developments in radiation curable (not aqueous) adhesives
adapted for use on cut and stack labelers referenced in
issued and pending patent applications to McNutt et. al.
15 have led to the development of more sophisticated
adhesive metering mechanisms and label wipers and
techniques that can be used to uniformly control adhesive
deposition and these modifications are contemplated for
use to apply the aqueous activation medium to the
20 activatable layer of the current invention at the minimum
possible level.

The techniques of U.S. 6,517,664 and U.S.6,663,746 which
are now being performed commercially and those developed
by McNutt et al use adhesives applied to the polymeric
25 film on the labeling machine to affix the label to the
container and work well for opaque labels. There are
still inconsistencies and imperfections in the
application of the adhesive such as bubbles and heavy or
light adhesive areas that when applied to clear or
30 contact clear substrates appear inferior when compared to
PSA labels where the adhesive has been pre-coated on the
substrate. In addition, the radiation curable adhesives
as defined by McNutt et. al. are very costly when
compared to aqueous systems and in comparison are health
35 and environmental unfriendly.

Accordingly, it is an object of the invention to provide

5 a polymeric label particularly adapted for use in post
mold wet applied labeling of polymeric, glass and metal
containers that has a dry non pressure sensitive
hydrophilic layer uniformly pre-applied that can be
activated into a defect free adhesive layer. This is
10 accomplished by pre-applying by coating, coextrusion or
extrusion the layer that is activated on the labeling
machine with an aqueous medium to become tacky and
function as an adhesive to affix the polymeric label to
the container. The activated label will readily feed from
15 the label magazine or gripper, adhere with sufficient
tack without moving through post labeling handling and
processing including but not limited to conveying,
filling, case packing and palletizing.

20 It is a primary object of the invention to provide a
polymeric label with a pre-applied hydrophilic layer
consisting of at least 30% dry by weight of animal glue
activated into an adhesive layer through an aqueous
medium on the labeler particularly adapted for use in
25 post mold wet applied labeling of polymeric and glass
containers that would have sufficient wet tack and
affinity for water, a water based solution or adhesive
used to allow for transfer of the water, water based
solution or water based adhesive to the polymeric label
30 substrate from the applicator roll(s), pad(s) or
pallet(s) of the labeling machine to activate it into an
adhesive.

It is also an object of the invention to provide an
35 activatable polymeric label for use in post mold wet
applied labeling of polymeric and glass containers that
would have a coefficient of expansion or contraction
under the conditions which the container sees which is

- 5 the same or compatible with that of the polymeric resin, glass or metal from which the container is made so that expansion and contraction of the container will not wrinkle or otherwise affect the integrity of the label.
- 10 It is also an object of the invention to provide a polymeric label for use in wet applied post mold labeling which would combine suitable properties of modulus of elasticity and flexibility and would not be degraded by handling and flexing of the subsequent container.
- 15 Finally, it would be desirable to provide a label for use in wet applied post mold labeling of polymeric containers which does not have to be removed from such containers in order to recycle or regrind defective or post consumer polymeric containers.

20 SUMMARY OF THE INVENTION

In considering the performance or economic shortcomings of prior art materials, I have discovered an improvement to the process as described in the pending and issued

25 applications by the applicant as cited above by which a polymeric label with a uniform pre-applied hydrophilic layer comprising at least 30% by dry weight of a animal glue can be applied to a container by activating the hydrophilic layer to form a tacky adhesive when wet on

30 the labeler by an aqueous medium before being applied to a glass, plastic or metal container or surface. The process may be carried out in a more consistent and uniform manner than a labeling process that uses a non activatable layer that requires a heavy adhesive layer

35 applied on the label machine to function. The method of the invention comprises:

- 5 (a) applying a uniform layer of a hydrophilic solid material containing at least 30% by dry weight of animal glue to a polymeric label based on the combined weight of the hydrophilic solid material and the weight of the animal glue and any additive, e.g. cross-linker,
10 and optionally drying said hydrophilic solid material to form an activatable hydrophilic layer on said polymeric label that can be activated into a tacky adhesive; (b) applying a light deposition water, water containing a cross-linking agent, a water based adhesive or a water
15 based adhesive containing a cross-linking agent over said activatable hydrophilic layer to form a tacky fastenable polymeric label free of bubbles and uneven adhesive streaks typical of the standard deposition of adhesives applied on aqueous labelers;
- 20 (c) fastening said fastenable polymeric label to a glass, plastic or metal container or surface; and
- (d) curing said polymeric label on said glass, plastic or
25 metal surface or container.

Containers labeled according to the process of the invention, where a cross-linker is present in the dried adhesive composition, are novel articles as they have a
30 label that has not been previously described.

For opaque or metalized labels, special mention is made that it is preferable to use a coextruded polymeric label substrate with a cavitated or voided adhesive surface producing micro-voids or pores on the adhesive side in
35 combination with a porous core. Typically these types of label substrates have a density <0.9 where the adhesive penetrates the rear plane of the label wherein said

5 polymer label contains a portion of said dried water
based adhesive within said micro-voided or cavitated
polymer label. These label substrates have a density
<0.9, preferably below 0.55 to 0.85 and more preferably,
from 0.6 to 0.75, and are made of polymers such as
10 polyethylene, polypropylene, polyester, i.e. polyethylene
terephthalate, polystyrene, polycarbonate, vinyl,
cellophane or compatibilized polymer blends which are
described in U.S. 6,517,664, which is incorporated by
reference.

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The use of the low density micro-voided polymer film can
allow portions of the water based adhesive to migrate
into the film during the drying cycle to provide an
enhanced bond between the polymeric label and the
20 container surface and to also impart stiffness to the
dried label on the container surface. Additionally, the
weak internal strength of the voided material provides
the appearance of superior bond when it is attempted to
remove the label because it fractures apart at minimal
25 force. Additionally, the pores create greater surface
area for bonding versus a polymeric film with a smooth
adhesive surface.

Most importantly, it has been found that voided
substrates with a porous adhesive side that are
30 judiciously applied with a hydrophilic layer on the
adhesive side show superior adhesion when rewet and
pressed onto the glass metal or plastic container because
the voided area or open area of the pore has a greater
surface area than a non voided smooth surface and appears
35 to act as a suction cup when the air in the cavitated or
voided area is pressed out as the label is applied
providing an improved bond while pulling activating
aqueous medium into the pores.

5 DETAILED DESCRIPTION OF THE INVENTION

Pre-applied activatable hydrophilic materials containing animal glue that can function as an adhesive are formulated so that their coefficients of expansion or contraction, thickness and modulus of elasticity when applied to a polymer film will result in a polymeric film facestock that will have hydrophilicity, absorbtivity, wet tack and drying properties that will permit the polymer film to be applied to polymeric, glass or metal containers via water based wet labeling techniques on standard paper labeling equipment.

It is contemplated that the pre-applied hydrophilic material will be dried on the polymeric substrate and rewetted at the time that the labeling material is applied to a container. It is also contemplated that the hydrophilic material may be applied at the time of labeling a container just prior to the time when the label is directly applied to a container without drying the hydrophilic material and rewetting the hydrophilic material at the time of labeling .The apparatus which is used to apply paper labels is well known to those in the art. The polymeric label substrate with the activatable hydrophilic layer will demonstrate sufficient "wet tack" during the label application period and the label drying period to permit containers to be handled and processed. The polymeric film based facestock will provide a label with printability, chemical and dimensional stability, resistance to cracking, tearing, creasing, wrinkling or any other degradation of the sort experienced by paper labels due to physical or environmental extremes.

The invention also permits the use of hydrophilic layer activatable by a water based solution into an adhesive to be used to fasten a clear or contact clear polymeric film substrate which is reverse printed and then over coated with the activatable hydrophilic layer to a

5 container. As used herein the reference to a "container" includes a surface of an object made of glass, plastic or metals such as bottles, cans, toys and building materials.

10 The activatable hydrophilic component or blends containing animal glue will be applied in the present invention to the selected polymeric sheet in a continuous or patterned layer to provide the absorptive, wet tack and drying properties that are necessary to enable
15 polymeric sheets to be successfully used as label substrates on polymeric or glass containers when activated through wetting with water, water and a cross-linker, adhesive or adhesive and a cross-linker using water based wet labeling techniques where the apparatus
20 is configured to apply the minimum amount of aqueous solution to activate the layer into a tacky adhesive when wet, but not excess aqueous medium to saturate the activatable layer causing it to loose its adhesive properties and not adhere well and take a long time to
25 dry. The activatable hydrophilic layer, containing at least 30% by weight of animal glue based on the weight of the hydrophilic solid material and the animal glue which may be applied by either a coating, coextrusion or an extrusion technique, has the function of absorbing
30 moisture to activate the layer as an adhesive when wet with an aqueous medium thus causing selected hydrophilic layers to function as an adhesive without any applied adhesive as is conventionally performed on aqueous labeling machines in the art or to activate by absorbing
35 the moisture from an aqueous adhesive if used, to cause the polymer film to adhere to the glass, plastic or metal container and to set up rapidly and positively. It is important or key to this invention to minimize the amount of aqueous medium used to activate the hydrophilic layer
40 as an adhesive. Excess activation moisture decreases the tack of the activated layer as it becomes saturated with moisture and will lead to longer drying times and loss of

5 adhesion properties. Additionally, the ability to
minimize machine applied imperfections such as bubbles
and streaks typical as previously mentioned in the
current art when heavy adhesive layers are applied on the
labeling machine is dictated by the amount of activating
10 medium used and if excess is used, it detracts from the
concept of a pre-applied defect free adhesively activated
hydrophilic layer.

It is also possible to coextrude the activatable
15 hydrophilic layer with the polymer film layer.

The choice of polymeric substrate for the label film will
determine the rigidity, deformability or conformability,
regrindability, printability and expansion or contraction
20 characteristics required for application to the selected
container without the problems associated with paper
labels.

In addition, the polymeric film substrate for the label
25 will be selected so that it will expand or contract to
the same degree as the container so that when ambient
conditions change, the label will not pucker or blister.

The polymeric materials include clear, opaque or colored
30 polypropylene, polyethylene, polyester, polystyrene,
polycarbonate, vinyl, cellophane or compatibilized
blends.

The term "film facestock" or "polymeric label substrate"
35 as used herein should be taken for purposes of the
present invention to refer to a material compatible in
terms of rigidity, deformability or conformability,
recyclability if a plastic container and expansion or

5 contraction characteristics with the plastic or glass
container to be labeled. Similarly, the "activatable
hydrophilic layer" previously mentioned has the
properties of minimal tack when dry so labels can be
unwound from a roll or separated from a stack and once
10 activated with moisture, it will have the properties of
wet tack, absorbtivity, drying, sufficient adhesion to
the polymeric label substrate and affinity and adhesion
to the container or labeling adhesive if used as an
activating medium in the wet or dry form.

15 Activatable hydrophilic layers containing at least 30%
animal glue can be wet or remoistened without adhesive
for use on a glass, plastic or metal container or a water
based adhesive can be used to activate and affix the
20 polymeric label substrate with the activatable
hydrophilic layer to the glass, plastic or metal
container. For deformable containers, the hydrophilic
layer activated into an adhesive is formulated to form a
bond with the container and the polymeric film substrate
25 such that when dry, the strength of the container wall-
hydrophilic adhesive interface and the cohesive strength
of the adhesive itself are all greater than the forces
required for deformation of the label.

30 As used herein and in the appended claims, the term
"hydrophilic" is used to describe materials or mixtures
of materials which bind, pass or absorb water. The term
"activatable hydrophilic layer" describes a hydrophilic
layer that when binding, passing or absorbing water
35 becomes activated and transforms into an adhesive layer
with wet tack and affinity for the container to be
labeled. The term activated as used herein describes the
change in a dry pre-applied dry hydrophilic layer on a

5 label substrate to a wet adhesive layer when activated with an aqueous medium that will adhere to the container wall to be labeled, dry and set up with strong adhesion.

The preferred "activatable hydrophilic" materials of the present invention are based on animal glue coating which in broad terms is an organic colloid of protein derivation from collagen which is a protein constituent of hide materials and bones obtained using well know techniques widely used to provide many commercially available glues. Hide animal glue is preferred over bone animal glue because of superior physical properties and strength. The animal source is not critical and glues may be derived from wild or domesticated animals such as horses, cattle, pigs, sheep and the like. Purified versions of animal glue are also known as gelatin. Animal glues are commonly graded on comparative gel gram strength values by manufacturers and provides a rough guide for use but this standard does not always measure their working qualities as adhesives for glass, plastic and metal containers. Considerations of gram strength, pH, ash content, clarity, grease content, type of glue (bone or hide), degree of purification and processing methods all have a bearing. The gram strength measurement of animal glue is also known as a gel strength measurement which ranges from about 30 grams (weak) to 500 grams (exceptionally strong) where the highest gram strengths contain greater amounts of reactive glue protein. Typically, stronger adhesive bonds are achieved with higher gram strength animal glues and blends of animal glues. Unfortunately, as gram strength increases, so does the dry brittleness of the glue which must be addressed in formulating using modifying components such

- 5 as plasticizers, humectants and modifying synthetic resin dispersions.

In physical form, dry animal glues are odorless, relatively tack free hard materials ranging in clarity
10 from light amber to dark brown depending on the origin, processing technique and degree of purification that contain 10 - 14% moisture. Almost all grades can be made up into aqueous solutions and many can be melted and applied at temperatures less than the boiling point of
15 water such as through a die or extruder as long as it is vented for potential moisture that could flash off. When aqueous formulations are prepared, the moisture content of the hard material is included in calculating the amount of water added to obtain the desired weight
20 percent dispersion in water of the animal glue. For a clear polymeric substrate, clarity or contact clarity of a thin activatable hydrophilic layer comprising at least 30% animal glue by dry weight dictates that relatively clear and pure animal glue is preferably used.

25 In water, solutions of animal glues based on hide which are typically the higher gram strength variety preferred for use in this invention instead of bone based glues are generally reaction neutral and have a pH range of 6.4 -
30 7.4 which is a pH that makes them compatible with many other materials. The specific gravity of dry animal glue is approximately 1.27.

An important feature of animal glue in the present
35 invention is that when dry animal glue is placed in cold water like an ice chest for beverages, animal glues do not dissolve readily but swell absorbing considerable water forming a gel state and must be heated to dissolve

5 into solution at 100 - 140 °F. The rapid development of
a gel state when wet with an aqueous medium provides a
fast set and tackiness with quick development of initial
bond and holding strength which is critical for the
successful application of polymeric labels to glass,
10 plastic and metal containers using wet labeling
techniques. For applications where long term contact with
water and subsequent swelling of the animal glue could
cause a loss of adhesion, it is preferred to crosslink
the animal glue to make it moisture resistant. One of the
15 keys to this invention is maintaining the beneficial
properties of non cross-linked animal glue for label
application using at least 30% animal glue in the
activatable hydrophilic layer which is then cross-linked
and rendered moisture resistant after application by the
20 water containing a cross-linker or adhesive containing a
cross-linker which is applied when the hydrophilic layer
is activated into an adhesive. High speed labelers run
from 200 - 1,200 container per minute and the cross-
linking reaction is relatively slow at even at high
25 levels of cross-linker so the layer can be wet, develop
tack and adhesion to the container to be labeled and cure
to moisture resistant over time. This time period varies
depending on the activatable layer formulation, cross-
linker of choice and amount of each component used along
30 with the amount of water that must be absorbed and dried.
The time period can run from 12 hours to 14 days but
stable formulations that are rendered moisture resistant
in 72 hours are adequate for most commercial labeling
applications. A key advantage of cross-linked activated
35 adhesives consisting predominantly of animal glue is that
when dry and rendered moisture resistant, the adhesive is
not impervious and hard and in fact the adhesive layer
will "give" or move slightly under high moisture

5 conditions and contact the surface to be labeled on
drying providing a "live" adhesive bond that takes up the
stresses and strains that normally occur under labeling
and drying conditions. Another key benefit of an adhesive
layer containing animal glue that forms a gel structure
10 is that if the surface to be labeled is cool, the animal
glue component will gel faster and set a bond faster
because it is less fluid. This can be an important factor
in brewery applications where post mold labeling of cold
beer or cold storage of labeled containers can accelerate
15 the bond of the activatable layer.

Another important feature of animal glue layers,
particularly those deposited from water or wet with water
is that when dry, they exhibit high adhesive strength,
20 are continuous, non-crystallizing, non-cracking and of
great strength and elasticity. Additionally, animal glue
is reaction neutral, relatively odorless, non toxic and
non corrosive. Due to its unique protein structure,
animal glue is not precipitated by acids or alkali's and
25 is resistant to structural breakdown by acids or alkali's
within normal practical limits so for use as a labeling
adhesive where the contents of a container could leak or
drip down the side of the container and attack the
adhesive, animal glue is durable. Animal glue based
30 adhesives are also resistant to grease, oil, alcohol and
other chemicals that are free of water and as stated
above, to overcome moisture sensitivity, animal glue can
be rendered moisture resistant by cross-linking.

35

For glass containers, it is preferred to use high gram
strength animal glues at a level of at least 50% dry by
weight of the activatable hydrophilic layer to achieve a

5 strong bond where the gram strength of the animal glue is greater than 50 grams and more preferably in the range of 175 - 225 grams. More preferably, for glass containers a dry level of animal glue between 60-80% is preferred as is a gram strength in excess of 175 grams (also known as
10 gel strength). The higher the gel strength of the animal glue, the stronger the adhesive bond to glass will typically be but also the more brittle the bond will become, especially after crosslinking so the 175 - 225 gram range while not limiting, is preferred for many
15 applications. Animal glue shows a specific affinity for glass and coated glass and is ideal as a base component to be formulated into an activatable hydrophilic adhesive layer because of its strong wet tack and affinity for glass. Animal glue has such a strong affinity for glass
20 that some formulations when dry and adhered to the glass will pull glass particles with it when removed. This has been proven by those that use animal glue to create chipped glass or frosted glass decorative designs using animal glue allowed to dry on glass that is subsequently
25 removed. This high affinity and bond strength to glass is why animal glue is the key component of this invention for activatable layers on polymeric films for high speed post mold labeling.

30 For plastic containers, it is recommended to blend synthetic acrylic polymers which bind or absorb water and become adhesives such as polyacrylic acid, polyacrylic acid copolymer or carboxylated sodium polyacrylate with the animal glue to promote adhesion to the plastic
35 container wall. For plastic containers, the dry animal glue level in the activatable layer can range from 30-80% but it is preferred at a level of 35-45% in combination with synthetic polymers. Moisture sensitive synthetic

5 polymers that can be rendered insoluble through cross-linking can be added at levels up to 70% dry polymer

Amounts of non moisture sensitive synthetic polymers can also be added as modifiers at levels up to 50% dry
10 polymer but most preferably at levels up to 25% dry polymer.

If synthetic polymers are used, they can be in the form of solutions, dispersions and emulsions but solution polymers are preferred.

15

In addition to synthetic resins as discussed above, animal glue solutions are compatible with select natural resins, modifying additives such as plasticizers, oils, fats, waxes along with other adhesive materials such as
20 casein, starch, dextrine and gums under certain conditions.

To plasticize and increase the flexibility of animal glue and control lay flat, humecants (plasticizers) such as
25 urea, polyethylene glycol, glycerin, sorbitol, cane or invert sugars or combinations of the preceding are added at levels up to 40% dry and most preferably 25-30% dry depending on the properties desired but preferably at levels < 30% if the activatable layer is subsequently to
30 be reacted (cross-linked), to be rendered resistant to moisture to minimize the level of non-reactive components in the matrix of the activatable hydrophilic layer. It is noted that urea acts as a gel dispersant to reduce the viscosity of the gel for coating applications while it is
35 inert in the animal glue matrix.

As discussed above, a preferred aspect of the present invention is to use cross-linkable (reactive) components

5 in the activating aqueous solution to react with the hydrophilic layer that converts into an adhesive that cures to become more moisture resistant as it dries and builds adhesion to the container wall. Not only does the cross-linking agent make the activated adhesive more
10 moisture resistant, it can provide greater initial wet tack versus using water only and promotes adhesion to the container wall while increasing chemical resistance to materials that may come in contact with the adhesive layer.

15 Examples of synthetic cross-linkable materials are those which contain carboxyl groups, hydroxyl groups or other functional group which will react with a cross-linking agent. The cross-linking agent can also be added to an
20 adhesive used to wet and activate the hydrophilic layer. When water and a cross-linking agent are combined, the composition will comprise 0.005 -10% by wt. of cross-linking agent. Preferred crosslinking agents are Polycup 172 from Hercules and Glyoxal available from BASF
25 Corporation.

The coated, extruded or coextruded activatable hydrophilic layer converts to a wet tacky adhesive layer when wet with an aqueous solution which is defined as a
30 substance capable of combining two surfaces by the formation of a bond. If a light deposition of an aqueous adhesive is used as the activating medium, the activatable hydrophilic layer bonds to the polymeric film substrate and the glass, metal or polymer of the
35 container wall when dry.

The use of the properly formulated activatable hydrophilic layer for a given polymeric labeling substrate and container to be labeled will have a direct

5 effect on the speed which the labeling line can be run.
When considering the choice of the activatable material
which forms the hydrophilic layer, which may be applied
by coating, coextrusion or extrusion, one must consider
the label substrate, container to be labeled, labeling
10 machinery, activation technique and down stream
processing requirements such as filling, conveying and
packing. In addition the final appearance of the label
such as the clear no label look or a plain opaque or
metalized label must be considered in the choice of the
15 components of the hydrophilic layer. Generally, a deposit
of from 0.25 to 8 lbs./3000 square feet of the
activatable hydrophilic layer, when dried, may be
employed on the polymeric film layer, depending on the
particular material that is selected and the method that
20 is used to apply the layer such as coating, coextrusion
or extrusion.

It is critical to the successful application and use of
an activatable hydrophilic polymeric film label to
25 control how the water or water based adhesive is applied
to the activatable hydrophilic layer, how deposition
(weight or thickness) is controlled and how the resultant
combination with the container is pressed together.
Generally, from <0.05 to 2.5 g. /sq. ft. of activating
30 medium (water or water based adhesive) is applied to the
pre-applied activatable hydrophilic layer with 100%
coverage of the label with a preferred range of 0.1-0.25
g. / sq. ft. If a grid or other pattern of activating
medium is employed, then the amount of activating medium
35 may be reduced. If a grid pattern is employed, the
hydrophilic layer may be applied to be substantially in
register with the activating medium.

5 It is critical to the successful application and use of
an activatable hydrophilic polymeric film label to
precisely control how the amount of aqueous activating
fluid medium (water, water plus a cross-linker, adhesive
or adhesive plus a cross linker) is applied. To much
10 aqueous medium for a given deposition of activatable
hydrophilic layer will overpower the layer and will
result in loss of tack and initial adhesion and will
result in labels 'swimming: or moving as the labeled
container is conveyed, filled or packed and will increase
15 the drying time of the activated layer to produce a firm
adhesive bond to the wall of the labeled container. Not
enough aqueous activating medium will not completely
develop the full adhesive properties of the activatable
layer and will result in poor bonds.

20 For optimum aqueous medium application control, optical
appearance and uniformity, it has been found that it is
preferable to use smooth applicator pallets to apply the
activating solution which for purposes of this invention
includes water, water plus a crosslinking agent, adhesive
25 or adhesive plus a crosslinking agent. The activating
solution is not limited to these components but will
include them as a major portion of the activating
solution with minor components such as biocides, wetting
agents, fragrances, humectants, defoaming agents,
30 viscosity modifiers and rheological modifiers also
contemplated.

In a preferred embodiment, conventional hard rubber,
metal or aluminum glue applicator pallets are modified by
35 adhering a compressible surface like a foam layer with a
smooth surface to the adhesive or activating side of the
pallet. This allows for intimate contact between the
applicator pallet and applicator metering roll when the

5 activating solution is applied to the compressible surface and for intimate contact between the wetted pallet and the hydrophilic layer when the wetted pallet with activating solution is pressed in intimate contact with the hydrophilic layer. Compression of the soft foam
10 like layer as it contacts the wetted applicator roll in contact with the activating solution is important as a means of uniformly controlling pick up of the activator solution. As detailed earlier, it is critical to control the deposition of the activating medium to a low level.

15 The compression of the foam modified pallet in combination with the gap adjustment of the applicator roll system allows for uniform metering and control of the activating solution. An added benefit is that the compression causes a wiping action as the compressible
20 surface of the applicator pallet rotates past the applicator roll to pick up the activating solution providing for a uniform application of solution where uneven application or even foam is smoothed out and made uniform.

25

When the wetted compressible pallet comes in contact with the activatable hydrophilic layer to pull the label out of the basket for application, the compressible pallet applies pressure on the hydrophilic layer and provides
30 for uniform application and wetting of the activatable hydrophilic layer to promote best optical clarity and ultimate adhesion of the label after drying.

The modified compressible surface must be smooth and
35 wettable which means the activating solution must wet out on the surface. In a preferred embodiment, the foam will compress at least 5% of its thickness for the optimum wiping action and will have a durometer of < 50. More

5 preferred is a compressability of about 5-50% of the
thickness of the foam of the applicator and preferably
>10% and a durometer of about 10-40 and preferably < 30
with a glass smooth surface. The type of compressible
foam like substance is not limiting but durable compounds
10 like silicone and urethane polymers are preferred.

As with any adhesive labeling technique, the type of bond
achieved is a fine balance between the container surface
to be labeled, the label material, adhesive formulation
15 which in this case is the activatable hydrophilic layer
in combination with the aqueous activating fluid and the
deposition of the activated adhesive. For purposes of
this invention, the adhesive layer is the combination of
the activatable hydrophilic formulation and the
20 activating medium whether it is water, water and a cross-
linking agent, adhesive or adhesive and a cross-linking
agent. The ultimate adhesion properties are controlled by
the surface characteristics of the material to be labeled
and the choice of adhesive layer formulation and
25 deposition of the adhesive layer

When using an adhesive or adhesive and cross-linker as
the activating fluid, it will generally be possible to
reduce the typical amount of adhesive applied to the
30 activatable hydrophilic layer of the label to an amount
which is <40% of the amount that is typically employed
for affixing paper labels to a surface and preferably
less than 20%. For example from 0.02 g. to 0.7 g. /sq.
cm. may be used for the preparation of labels
35 manufactured from polymeric films with a thickness range
from 1.5 to 8 mils.

5 The choice of the adhesive layer made up of the
activatable hydrophilic layer and activating medium, the
type of label substrate and container to be adhered
together, the plant processing conditions after labeling,
storage requirements and the end use requirements that
10 must be met such as high temperature resistance, ice
proofness or passing a 24 - 72 hour ice bath soak are
important considerations. There are many more specific
variables within these considerations all of which
influence the formulation of the proper activatable
15 hydrophilic layer and activating medium for a specific
application.

The bonding of the activatable layer can be accomplished
with mechanical (non smooth surfaces) and specific
20 adhesion. It has been found that the preferred animal
glue component of the activatable layer provides superior
adhesion characteristics when the layer is activated by
water or a water based adhesive containing a cross-
linking agent or a combination of cross-linking agents
25 such as zirconium salts of mineral acids, such as Bacote
20 from Magnesium Elektron, Inc., water soluble
polyamide-epichlorohydrin material such as Polycup 172
from Hercules, Glyoxal available from BASF Corporation or
an aldehyde donor such as Glutaraldehyde that rapidly
30 cross-links the animal glue and the like which may be
used at a level of 0.01-8% by weight of the activatable
layer composition.

Mechanical adhesion is defined as the bonding between
surfaces in which the adhesive holds the parts together
35 by inter-locking action and actual physical penetration.
Specific adhesion is the bonding between surfaces which
are held together by molecular forces wherein the
surfaces are non porous and no penetration is possible.

5 These forces are related to the polarity and size of the molecules, pore size of non smooth surfaces and the initial action in obtaining a bond when the activated surface is wet, becomes tacky and a bond develops through molecular forces.

10

In mechanical as well as specific adhesion, the activated hydrophilic layer must "wet" both surfaces completely or weak bonded areas will develop as it dries or "sets" resulting in a poor bond. Not only is wetting of the surfaces critical, penetration is also important and this is why a polymeric film that is cavitated, voided or porous on the activatable side is a preferred embodiment of the invention in combination with the activatable hydrophilic layer which is penetrated to a degree by the aqueous activating medium. Penetration is important since most combinations of surfaces to be adhered together involve at least one porous or absorptive surface which controls the "setting" characteristics. The preferred low density polymeric labels are made of polypropylene which is commercially available. The preferred density is 0.45 to 0.85; an especially preferred density is 0.50 to 0.65, as distinguished from the conventional polypropylene label stock which has a density above 0.9. These materials are sometimes referred to as cavitated, micro voided or foamed polypropylene. Other polymers which may be used include polyethylene, polyester, polystyrene, cellophane, polycarbonate or compatibilized polymer blends. It is preferred to utilize a low density polymeric label substrate in conjunction with a hydrophilic material such as the activatable hydrophilic layer on the polymeric label to allow for more rapid escape of water from the activating medium that is placed on the activatable hydrophilic layer on the back or

5 adhesive side of the low density polymeric label. One
common technique to create cavitation or voids in a
stretched polymeric film is to use incompatible particles
that separate and create a void or pore as the polymeric
film is stretched. A common particle used for creating
10 cavitation or pores is calcium carbonate and animal glues
have a strong affinity and bond for calcium carbonate
that is typically found in many voided polymeric film
layers the activatable adhesive composition will be
applied to so it will have superior adhesion.

15

For non porous polymeric film substrates, to facilitate
wetting of the surface and penetration, the activatable
hydrophilic layer and activating fluid that combine into
the adhesive must wet out the surface of the container to
20 be labeled. This is accomplished by applying the
activating medium to the selected activatable hydrophilic
layer which when applied to the container to be labeled
brings the hydrophilic layer activated into an adhesive
and container wall into intimate molecular contact. By
25 using an aqueous fluid activating medium that wets and
penetrates the hydrophilic layer as well as the container
surface, a fluid region is created that flows to cover
the surface as completely as possible. This is critical
to the invention where even an apparently smooth surface
30 in reality is composed of a random network of hills and
valleys. When the activated hydrophilic layer is in the
wet condition, it serves as a wetting bridge to promote
adhesion. The more rapidly the activated hydrophilic
layer can be applied (pressed in intimate contact with
35 the surface to be labeled), the greater the fluid region
will be before the activating medium is absorbed into the
hydrophilic layer, the better the wetting at the adhesive
interface will be resulting in stronger ultimate bonds

5 and improved optical clarity if a clear film is used.

As previously mentioned, various commercially available natural polymer based products at significantly reduced coat weight can be used as an additive to the animal glue
10 or in the aqueous activating medium with activatable hydrophilic layers to provide good adhesion of polymeric film layers to a plastic or glass surface. These materials include starch based adhesives or casein based adhesives now predominantly used for glass applications
15 since they do not bond well to plastic or metal. Synthetic polymer based materials that may be employed are commercially available and include EVA based materials which have free carboxyl groups, converted starch solutions, PVA based adhesives, synthetic resin
20 dispersions for metal or plastic containers or blends of synthetic and starch and/or casein based products and the like. Acrylic and acrylic/methacrylic polymer dispersions may also be used as synthetic polymer additives. Optionally, if just water or water and a cross-linking
25 agent are used as the activating medium, it is preferred to thicken the water or solution for better machining on the labeler that is designed to handle higher viscosity mediums such as conventional labeling adhesives by adding a thickening amount of a thickener. Many commercially
30 available thickeners can be used but special mention is made of the Laponite family of synthetic thickeners from Southern Clay Products that form a gel structure of an aqueous solution at low addition levels that will not overpower the adhesive properties of the activated medium
35 and will not interfere with the ultimate bond or moisture sensitivity of the dry adhesive at the low levels used to thicken the aqueous solution. Aluminum silicate or other well known natural or synthetic gums may also be added.

5 It is clear that one specific activatable hydrophilic layer may not fit all applications but it has been found that the activatable hydrophilic layers of the present invention can be tailored to particular applications based on the conditions and requirements for wet PML
10 labeling of polymeric substrates but the activatable layer must contain at least 30% by weight of the dry activatable layer of animal glue that when activated (wet) by an activating fluid medium becomes sufficiently tacky to adhere a polymeric layer to a container through
15 filling, conveying, processing or packing that will subsequently dry and provide good adhesion to the container. When working with natural and synthetic activatable layers that are obviously sensitive to moisture, it is important depending on the moisture
20 sensitivity of the formulation to add a humectant to the activatable layer at a level of 0.25-25% by dry weight to provide curl resistance and to impart lay flat properties to the polymeric film labels. The humectants also tend to act as plasticizing agents so the activatable layer does
25 not become too brittle when dry and include urea, polyethylene glycols such as PEG400, polyvinyl alcohol, glycerin, sorbitol and the like.

For a coextruded product, if an adhesion promoting tie
30 layer is employed, materials such as maleic anhydride, ethyl acrylic acid and the like may be employed at levels up to 5% by weight of the hydrophilic composition. For a coated product, if a primer is employed, materials such as chlorinated polypropylene, polyethylene imine (PEI),
35 acrylic primers and the like may be employed at levels of 0.05-1.0 lbs/3000 sq. ft. Special mention is made of acrylic resin based primers that are filled with a silicate such as colloidal silica also known as "water

- 5 glass" that has demonstrated superior adhesion characteristics to animal glue that has a high natural affinity for glass and silicates such as alkali metal silicates.
- 10 Slip aids and anti-blocking compounds commonly used in the art can prevent excessive friction between the activatable hydrophilic layer and the printed label face and also control the effect of ambient moisture levels which may tend to cause label blocking and interfere with
- 15 the operation of high speed automated machinery which is used to apply labels. These materials may be used at a level of 0.05-5% by weight of the activatable layer composition and/or the protective over coat applied over the printed indicia on the side of the label opposite the
- 20 activatable layer and include materials such as microcrystalline wax emulsions, erucamide dispersions, polytetrafluoroethylene compositions, silicone beads, modified silicone solutions, parafin wax emulsions, high melting polypropylene emulsions, carnauba wax emulsions,
- 25 oxidized ethylene/EVA compositions, micronized polyethylene wax/PTFE emulsions, micronized polypropylene, micronized fluorocarbons such as PTFE (Teflon), micronized polyethylene, silica and talc. Specific mention is made of the use of silanes to
- 30 partially crosslink the animal glue in the coating matrix effectively reducing the surface moisture sensitivity of the coating to help prevent blocking and to create a more crystalline surface for improved slip. Of specific note are the Gransil series of silane crosslinkers available
- 35 from Grant Chemical, Paterson NJ and specifically Gransil 51 which is a γ -glycidoxypropyl-trimethoxy silane. A preferred defoamer is polypropylene glycol having a weight average molecular weight of about 200-600.

5 The wetting agent may comprise a non-ionic surfactant such as an ethoxylated nonyl phenol or an ethoxylated amine such as surfynol from Air Products & Chemicals Corporation.

10 It is contemplated that the activatable hydrophilic layer can be applied in multiple coating steps to have a base layer with humectants for curl control that is very reactive to moisture and would tend to block with an overcoat of a less moisture sensitive layer that can be crosslinked that will resist blocking where the base
15 layer will comprise from 50-90% of the total layer coat weight.

Protective coatings may be used to protect the exposed polymer film and printed indicia of the label when
20 applied at a level of 0.25-4 lbs./3000 sq. ft. using conventional application techniques. These materials include styrenated acrylics such as OC1043 from O.C. Adhesives Inc., urethanes such as AS455 from Adhesion Systems Inc., Flexcon Release Varnish from Flint Ink. In
25 a preferred embodiment, a protective coating with release (non stick) characteristics commonly known in the art is preferred as the protective overcoat to prevent blocking if the stacks of labels are exposed to moisture.

30 If an antistatic agent is employed in the printable overcoat applied over the indicia, it may be present at a level of 0.5-3% by weight of the dry coating. These materials include quaternary ammonium salts such as Ethaquad C12, sulfonated styrene maleic anhydride,
35 sulfonated polystyrene, sulfonated vinyl toluene maleic anhydride, conductive polymers and organo modified silicones such as Silwet L77. It is noted that anti-static agents are typically not needed in the activatable

- 5 layer because the high moisture content of the animal glue provides exceptional static elimination properties.

Optionally, if a metalized coating of a thin metal film is deposited on the polymeric sheets or rolls, premium
10 quality decorative labels with all of the advantages set forth above will be provided.

It is clear that one specific activatable hydrophilic layer may not fit all applications but hydrophilic layers
15 can be tailored to particular applications based on the conditions and requirements for wet PML labeling of polymeric substrates.

If an adhesion promoting tie layer or primer is employed
20 to promote hydrophilic layer adhesion or adhesive adhesion, materials such as maleic anhydride, ethyl acrylic acid, carboxylated polyurethane resin and the like may be employed at levels of 0.1-3 lb/3,000 sq. ft.

25 If a cross-linking catalyst is added to the adhesion promoting tie layer, the ratio of catalyst to adhesion promoting tie layer may be an amount that is sufficient to cure the adhesion promoting tie layer. An excess of the catalyst, i.e. 5-25% in excess of the amount of the
30 catalyst that is required to cure the adhesion promoting tie layer may be used to provide a portion of the catalyst at the interface of the adhesion tie promoter and the hydrophilic layer to increase the moisture resistance of the hydrophilic layer without decreasing
35 the moisture absorbtivity of the hydrophilic layer. Additionally, excess catalyst can also be available to aid in curing of the adhesive.

- 5 The following formula may be utilized for preparing a layer which, after drying, may be utilized as label stock when treated with a suitable activating solution.

ACTIVATABLE HYDROPHILIC LAYER FORMING SOLUTION

- 10 Animal Glue 30-95wt% preferably 45-60wt%
Synthetic Or Natural Polymers 5 - 65wt%, preferably 40-55wt%
Cross-linker 0-5wt%, preferably , <2wt%
Humectants 0-15wt%, preferably 5-10wt%
15 Wetting Agent 0-1wt%, preferably <0.5wt%
Defoamer 0-1wt% preferably <0.5wt%
Anti-block Additives 0-2wt %, preferably <1wt%
Slip Additives 0-2wt %, preferably <1wt%
Water balance to 100wt%

20

As noted above, different lots of animal glue in the "dry" state have different levels of retained moisture so that each batch will vary in the content of added water due to the varying water content of the different lots of
25 animal glue.

- When a glass substrate is to be labeled, higher levels of animal glue are generally required. When a plastic surface is to be labeled, higher concentrations of added
30 synthetic polymers are generally required.

The following describes an activating solution which may be used in the practice of the invention:

35 ACTIVATING SOLUTION

- Cross-linker 0-10wt%, preferably 1-10wt%; especially preferably, 2-4wt%
Wetting Agent 0-1wt%, preferably <0.5wt%
40 Defoamer 0-1wt% preferably <0.5wt%
Thickener 0-2wt%, preferably <1wt%
Natural Polymers 0-15wt%, preferably 5-10wt%
Synthetic Polymers 0-10wt%, preferably <5wt%

5 Water balance to 100%

The following examples illustrate the invention.

Defined terms and tests are as follows:

10

Wet Tack, - this is a measure of the initial adhesion of the label to a surface immediately after activation and application to the surface and evaluated by trying to push or slide the label on the surface it was applied to.

15

Ice Soak - Submersion of the labeled sample in an ice water/cold water bath at a temperature of about 33-38° for 72 hours. After 72 hours, the labeled article is rotated in the bath and labels are evaluated for edge flagging or removal.

20

Edge Difficulty - this is a measure of the degree of difficulty to lift the edge of the sample after it has been allowed to dry and cure for a specified time period.

25 W denotes wet test after ice soak, D denotes dry test.

Adhesion Rating - this is a measure of the degree of bond of the label to the surface when it is peeled back in a slow continuous motion by hand and is performed right after the edge difficulty test. If an ice soak test is performed, this test is performed on sample pre and post ice soak test.

30

Adhesive Action - defines whether the activatable layer splits, stays with the label or transfers to the labeled surface after the label is peeled back for the adhesion rating test. If an ice soak test is performed, this test is performed on sample pre and post ice soak test.

35

5

Curl - curl is defined as the degree the edges of the label specimen lift when exposed to changing environmental conditions in terms of temperature and humidity.

10

Blocking - is defined as the degree of tack versus separation of individual labels when the coated side of the label is in contact with the opposite side in a constant humidity chamber (92% RH) for 24 hours at room temperature. Since different films are used, for comparative test purposes the non adhesive side was always evaluated against the same Flexcon varnish from Flint Ink.

15

20 All tests except Adhesive Action are rated on a scale of 0 to 3 where 0 is failure, 1 is poor, 2 is good and 3 is excellent. Adhesive Action is denoted as A for split, B stays on label, C transfers to substrate to be labeled.

25

The term Sample Formulation describes the formulation of the activatable layer. The particular source of the animal glue is not critical and the key property of adhesion is specified as "gram strength". Materials denoted ACW are moisture absorbing acrylic polymers available from Noveon.

30

35 Approximate Coat Weight - is the theoretical coat weight based on the solids of the coating and draw down rod size in grams/ MSI MSI = 1000 sq.in. To convert to metric

5 equivalent, multiply grams / MSI x 1.55 for grams / sq.
meter

Type Of Film Used - PET denotes clear polyester - 2
mil Shimpex

10

OPP denotes 2 mil clear oriented
polypropylene 196LL from
ExxonMobil or TL50 from Inteplast

15

WOPP denotes 3.4 mil white cavitated
oriented polypropylene 85LP from
ExxonMobil

20

OPS denotes 2 mil oriented polystyrene
from Alcoa Kama

All films were corona or flame treated to enhance
adhesion. Corona treatment is a process which utilizes a
voltage source, an electrode, a dielectric and a ground.
25 High voltage is applied to the electrode and the
dielectric is placed between the electrode and the
ground. The dielectric comprises the substrate, an
insulator, such as a silicone or a ceramic and air. The
voltage buildup on the electrode ionizes the air in the
30 electrode/substrate gap, causing the formation of highly
energized corona which excites the air molecules,
reforming them into a variety of free radicals which then
bombard the substrate surface increasing its polarity by
distributing free bond sites across it. The treater may
35 use a dielectric covered roll or a bare-roll which uses a
dielectric covered electrode. a system for corona
discharge treatment may comprise a modified corona
treater such as Model AB1977 using a power supply Model

- 5 No. AB6628, both of which are available from Pillar Technologies, Inc., Heartland WI.

Surface Labeled - G denotes glass, PET denotes polyester, HDPE denotes High Density Polyethylene

10

The technique to prepare samples is as follows: .

- 1 - Prepare Activatable Hydrophilic formulation
- 15 2 - Draw down Activatable formulation on selected film substrate
- 3 - Dry in forced hot air oven
- 4 - Prepare Activator Solution
- 5 - Apply Activator Solution with foam pad or brush to
- 20 activate with the minimum amount of solution to activate the coating
- 6 - Rapidly apply the activated label to the surface to be labeled
- 7 - Allow the applied label to dry/cure for 7 days.

25

All coating and activator formulations are specified in parts by weight per 100 parts of composition and refer to dry parts of components except water.

5

Example 1

10 Activatable Hydrophilic

Formulation - 30 parts 192 gram strength Animal Glue
 5 parts Urea
 5 parts Glycerine
 60 parts water

15 Film Type - PET

Approx. Coat Weight - 4.5 grams/MSI

Activator Formulation - 1 part Polycup 172
 1 part Glyoxal
 98 parts water

20

Substrate To Be Labeled - G

25 Wet Edge Difficulty Adhesion Rating Adhesive Action
 Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice
Soak

3 3* / 2 3 / 2 A / A

30 * - film begins to destruct

Curl Blocking Ice Soak

3+ 2 3

35

Example 2

40 Activatable Hydrophilic

Formulation - 30 parts 192 gram strength Animal Glue
 5 parts Urea
 5 parts Glycerine
 59.8 parts water
 0.2 parts Silane Crosslinker Gransil 51

45

Film Type - PET

Approx. Coat Weight - 4.5 grams/MSI

50 Activator Formulation - 1 part Polycup 172
 1 part Glyoxal
 98 parts water

Substrate To Be Labeled - G

55

5	Wet Edge Difficulty Adhesion Rating Adhesive Action			
	<u>Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice</u>			
	<u>Soak</u>			
10	3	2 / 2+	3 / 3	A / A
	<u>Curl Blocking Ice Soak</u>			
15	2	3	3	

Example 3

20	Activatable Hydrophilic			
	Formulation - 30 parts 192 gram strength Animal Glue			
	5 parts Urea			
	5 parts Glycerine			
25	59.8 parts water			
	0.2 parts Silane Crosslinker Gransil 51			
	Film Type - OPP			
	Approx. Coat Weight - 4.5 grams/MSI			
30	Activator Formulation - 1 part Polycup 172			
	1 part Glyoxal			
	98 parts water			
35	Substrate To Be Labeled - G			

	Wet Edge Difficulty Adhesion Rating Adhesive Action			
	<u>Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice</u>			
	<u>Soak</u>			
40	3	3 / 2	2+ / 1+	C / C
	<u>Curl Blocking Ice Soak</u>			
45	1+	3	3	

Example 4

50	Activatable Hydrophilic			
	Formulation - 30 parts 192 gram strength Animal Glue			
55	5 parts Urea			

- 5 5 parts Glycerine
 59.8 parts water
 0.2 parts Silane Crosslinker Gransil 51
- Film Type - OPS
- 10 Approx. Coat Weight - 4.5 grams/MSI
- Activator Formulation - 1 part Polycup 172
 1 part Glyoxal
 15 98 parts water
- Substrate To Be Labeled - G
- 20 Wet Edge Difficulty Adhesion Rating Adhesive Action
 Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice
 Soak
 3 3 / 2* 2+ / 2 A / C
- 25 * Film Splits
- Curl Blocking Ice Soak
 3 3 3
- 30

Example 5

- 35 Activatable Hydrophilic
 Formulation - 30 parts 192 gram strength Animal Glue
 2.5 parts Urea
 2.5 parts Glycerine
 40 64.9 parts water
 0.1 parts Silane Crosslinker Gransil 51
- Film Type - OPP
- Approx. Coat Weight - 3.2 grams/MSI
- 45 Activator Formulation - 1 parts Polycup 172
 1 parts Glyoxal
 98 parts water
- 50 Substrate To Be Labeled - G
- Wet Edge Difficulty Adhesion Rating Adhesive Action
 Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice
 55 Soak

$$5 \quad 3 \quad 3+ / 3^* \quad 2 \quad A / A$$

* - Film begins to randomly destruct

Curl Blocking Ice Soak

3 2 3

Example 6

Activatable Hydrophilic

Formulation - 30 parts 192 gram strength Animal Glue

2.5 parts Urea

2.5 parts Glycerine

64.9 parts water

0.1 parts Silane Crosslinker Gransil 51

25 . Film Type - WOPP

Approx. Coat Weight - 3.2 grams/MSI

Activator Formulation - 1 part Polycup 172

1 part Glyoxal

30 98 parts water

98 parts water

Substrate To Be Labeled - G

35 Wet Edge Difficulty Adhesion Rating Adhesive Action

[illegible]

Soak

$$\frac{3+}{3} \quad 3 / 2 \quad 2+ / 2 \quad C / C$$

40 Curl Blocking Ice Soak

$$2+ \quad 2 \quad . \quad 3$$

Example 7

Activatable Hydrophilic

Formulation - 30 parts 192 gram strength Animal Glue

50 5 parts Urea

5 parts Glycerine

60 parts water

Film Type - PET

Approx. Coat Weight - 2.5 grams/MSI

- 5 Activator Formulation - 1 part Polycup 172
 1 part Glyoxal
 98 parts water

Substrate To Be Labeled - G

10

Wet Edge Difficulty Adhesion Rating Adhesive Action
Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice
Soak

15

3 3 / 2 2.5 / 1.5 A / C

Curl Blocking Ice Soak

20

3 2 3

Example 8

25

Activatable Hydrophilic
 Formulation - 30 parts 192 gram strength Animal Glue
 5 parts Urea
 5 parts Glycerine
 60 parts water

30

Film Type - PET
 Approx. Coat Weight - 7.2 grams/MSI

35

Activator Formulation - 1 part Polycup 172
 1 part Glyoxal
 98 parts water

Substrate To Be Labeled - G

40

Wet Edge Difficulty Adhesion Rating Adhesive Action
Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice
Soak

3 3 / 3 3 / 3 A / A

45

Curl Blocking Ice Soak

2+ 1 3

50

Example 9

- 55 Activatable Hydrophilic
 Formulation - 30 parts 192 gram strength Animal Glue

5 5 parts Urea
 5 parts Glycerine
 59.8 parts water
 0.2 Silane Crosslinker Gransil 51

Film Type - PET

10 Approx. Coat Weight - 7.2 grams/MSI

 Activator Formulation - 1 part Polycup 172
 1 part Glyoxal
 98 parts water

15 Substrate To Be Labeled - G

 Wet Edge Difficulty Adhesion Rating Adhesive Action
 Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice
 20 Soak

 3 3 / 3 * 3 / 3 A / A
 * - Film Destructs

25 Curl Blocking Ice Soak

 1 3 3

 Example 10

30

 Activatable Hydrophilic
 Formulation - 30 parts 192 gram strength Animal Glue

35 2.5 parts Urea
 2.5 parts Glycerine
 64.9 parts water
 0.1 parts Silane Crosslinker Gransil 51

40 Film Type - OPP
 Approx. Coat Weight - 4.5 grams/MSI

 Activator Formulation - 1 part Polycup 172
 1 part Glyoxal

45 88 parts water
 10 parts sucrose

 Substrate To Be Labeled - G

50

 Wet Edge Difficulty Adhesion Rating Adhesive Action
 Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice Soak

55 3 3+ 3 3 / 2 C / C

5

<u>Curl Blocking</u>	<u>Ice Soak</u>
3	2 3

Example 11

10

Activatable Hydrophilic

Formulation - 30 parts 192 gram strength Animal Glue
 15 2.5 parts Urea
 2.5 parts Glycerine
 64.9 parts water
 0.1 parts Silane Crosslinker Gransil 51

20 Film Type - OPP

Approx. Coat Weight - 2.2 grams/MSI

Activator Formulation - 1 part Polycup 172

1 part Glyoxal
 25 88 parts water
 10 parts sucrose

Substrate To Be Labeled - G

30

Wet Edge Difficulty Adhesion Rating adhesive Action

<u>Tack</u>	<u>Pre/Post Ice Soak</u>	<u>Pre/Post Ice Soak</u>	<u>Pre/Post Ice Soak</u>
2	2+ 1+	2 / 1+	C / C

35

<u>Curl Blocking</u>	<u>Ice Soak</u>
3	2+ 3

40

Example 12

Activatable Hydrophilic

45 Formulation - 30 parts 150 gram strength Animal Glue
 5 parts Urea
 5 parts Glycerine
 60 parts water

Film Type - OPP

50

Approx. Coat Weight - 4.5 grams/MSI

Activator Formulation - 2 part Polycup 172

2 part Glyoxal
 55 96 parts water

5

Substrate To Be Labeled - G

10 Wet Edge Difficulty Adhesion Rating Adhesive Action
 Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice
 Soak
 3+ 3 / 2+ 2+ / 2 C / C

15 Curl Blocking Ice Soak
 3 2 2+

Example 13

20

Activatable Hydrophilic

Formulation - 30 parts 400 gram strength Animal Glue

5 parts Urea

5 parts Glycerine

25

60 parts water

Film Type - PET

Approx. Coat Weight - 4.5 grams/MSI

30

Activator Formulation - 2 part Polycup 172

2 part Glyoxal

96 parts water

Substrate To Be Labeled - G

35

40 Wet Edge Difficulty Adhesion Rating Adhesive
 Action
 Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice
 Soak
 3+ 2+ / 2 2 / 2* C / C

* - Observed very crystalline and fractures easily

45 Curl Blocking Ice Soak
 1+ 3 3

Example 14

50

Activatable Hydrophilic

Formulation - 30 parts 192 gram strength Animal Glue

55

5 parts Polyethylene Glycol

5 65 parts water
Film Type - PET
Approx. Coat Weight - 4.5 grams/MSI

10 Activator Formulation - 1 part Polycup 172
 1 part Glyoxal
 88 parts water
 10 parts sucrose

Substrate To Be Labeled - G

15 Wet Edge Difficulty Adhesion Rating Adhesive Action
Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice
Soak

20 3 3 / 2 3 / 2 A / A

* - film begins to destruct

25 Curl Blocking Ice Soak

3 3 3

Example 15.

30

Activatable Hydrophilic

35 Formulation - 40 parts 192 gram strength Animal Glue
59.8 parts water
0.2 parts Polypropylene Glycol

40 Film Type - PET
Approx. Coat Weight - 4.5 grams/MSI

Activator Formulation - 1 part Polycup 172
1 part Glyoxal
98 parts water

45 Substrate To Be Labeled - G

Wet	Edge	Difficulty	Adhesion Rating	Adhesive Action
1	2	3	4	5
6	7	8	9	10
11	12	13	14	15
16	17	18	19	20
21	22	23	24	25
26	27	28	29	30
31	32	33	34	35
36	37	38	39	40
41	42	43	44	45
46	47	48	49	50
51	52	53	54	55
56	57	58	59	60
61	62	63	64	65
66	67	68	69	70
71	72	73	74	75
76	77	78	79	80
81	82	83	84	85
86	87	88	89	90
91	92	93	94	95
96	97	98	99	100

50	Tack	Pre/Post	Ice	Soak	Pre/Post	Ice	Soak	Pre/Post	Ice
----	------	----------	-----	------	----------	-----	------	----------	-----

$$3 \qquad 3 / 2 \qquad 3 / 2 \qquad A / A$$

* - film begins to destruct

55

5

Curl Blocking Ice Soak

2 2 3

10

Example 16

15

Activatable Hydrophilic

Formulation - 30 parts 192 gram strength Animal Glue

5 parts Urea

5 parts Glycerine

20

60 parts water

Film Type - PET

Approx. Coat Weight - 4.5 grams/MSI

25

Activator Formulation - 5 parts Polycup 172

5 parts Glyoxal

90 parts water

Substrate To Be Labeled - G

30

Wet Edge Difficulty Adhesion Rating Adhesive Action

35

Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice Soak

3 2 / 2 1+ / 1+ A / A

40

Curl Blocking Ice Soak

3 2 3

45

Example 17

50

Activatable Hydrophilic

Formulation - 35 parts 400 gram strength Animal Glue

2.5 parts Urea

2.5 parts Glycerine

60 parts water

55

Film Type - PP

5

Approx. Coat Weight - 2.5 grams/MSI

Activator Formulation - 1 part Polycup 172
 1 part Glyoxal
 10 0.1 parts Gluteraldehyde
 97.9 parts water

Substrate To Be Labeled - G

15

Wet Edge Difficulty Adhesion Rating Adhesive Action
Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice
Soak

3 2 / 1+ 2 / 1+ C / C
 20 * - Observed very crystalline and fractures easily

Curl Blocking Ice Soak
 3 2+ 3

25

Example 18

30

Activatable Hydrophilic
 Formulation - 15 parts 400 gram strength Animal Glue
 15 Parts ACW97-19 Acrylic Resin
 70 parts water

35 Film Type - PET
 Approx. Coat Weight - 4.5 grams/MSI

Activator Formulation - 2 parts Polycup 172
 2 parts Glyoxal
 40 96 parts water

Substrate To Be Labeled - PET

45

Wet Edge Difficulty Adhesion Rating Adhesive Action
Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice
Soak

50 3 2 / 1 1+ / 1 A / B

Curl Blocking Ice Soak
 55

5 3 2 2

Example 19

10

Activatable Hydrophilic

15 Formulation - 15 parts 400 gram strength Animal Glue
 15 Parts ACW97-19 Acrylic Resin
 70 parts water

Film Type - PET

Approx. Coat Weight - 4.5 grams/MSI

20

Activator Formulation - 2 parts Polycup 172
 2 parts Glyoxal
 96 parts water

25 Substrate To Be Labeled - HDPE

30 Wet Edge Difficulty Adhesion Rating Adhesive Action
TackPre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice Soak

3 2 / 1 1+ / 1 B / B

35

Curl Blocking Ice Soak

3 2 2

40

Example 20

45

Activatable Hydrophilic

Formulation - 10 parts 400 gram strength Animal Glue
 20 Parts ACW97-20 Acrylic Resin
 70 parts water

50

Film Type - PET

Approx. Coat Weight - 4.5 grams/MSI

Activator Formulation - 2 parts Aziridine
 98 parts water

55

5 Substrate To Be Labeled - PET

10 Wet Edge Difficulty Adhesion Rating Adhesive Action
Tack Pre/Post Ice Soak Pre/Post Ice Soak Pre/Post Ice
Soak

15 3 2+ / 1+ 2 / 1+ B/ A

Curl Blocking Ice Soak

20 3 2 2